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Effect of the Quantity and Duration of Application of Simulated Acid Precipitation on Nitrogen Mineralization and Nitrification in a Forest Soil

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16. ABSTRACT
A study was conducted of the influence of the rate of application of simulated acid rain on N mineralization and nitrification in a forest soil. The rates were varied by applying different quantities of simulated rain for varying periods of time. The soil was exposed in the laboratory to simulated rain at pH 3.5, 4.1, or 5.6 at rates equivalent to 1.5,2.3,4.6, 7.1 or 15 times the average rate of precipitation in the field and then mineralizaton of soil N or oxidation of added ammonium was determined. The rates of N mineralization were inhibited by precipitation at pH 3.5 or 4.1 when applied for 27-234 day at rates 1.5 times greater than that which occurs in nature. N mineralization was not affected by simulated rain at pH 3.5 or 4.1 in soils exposed for 156 day at 2.3 times the natural rate of precipitation, for 27 or 81 day at 4.6 times the natural rate, for 54 day at 7.1 times the natural rate, or for 234 day at 15 time the natural rate. On the other hand, mineralization was fastest in soil exposed to pH 3.5 (234 day) at 4.6 times the natural rate of precipitation and for 81 day at 15 times natural rate. Nitrate formation in soil amended with ammonium was inhibited by rain of pH 3.5 regardless of the intensity of rain or duration of exposure. For a constant rate of rain application, the inhibition of nitrate formation in ammonium-amended soil generally increased with longer periods exposure. The data show that the use of different rates of additions of artifical rain or different periods of exposure to the simulated precipitation will lead to different conclusions on the influence of acid rain on N mineralization in soil.

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EFFECT OF THE QUANTITY AND DURATION OF APPLICATION OF SIMULATED ACID PRECIPITATION ON NITROGEN MINERALIZATION AND NITRIFICATION IN A FOREST SOIL

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Abstract. A study was conducted of the influence of the rate of application of simulated acid rain on N mineralization and nitrification in a forest soil. The rates were varied by applying different quantities of simulated rain for varying periods of time. The soil was exposed in the laboratory to simulated rain at pH 3.5, 4.1, or 5.6 at rates equivalent to 1.5, 2.3, 4.6, 7.1 or 15 times the average rate of precipitation in the field, and then mineralization of soil N or oxidation of added ammonium was determined. The rates of N mineralization were inhibited by precipitation at pH 3.5 or 4.1 when applied for 27 to 234 day at rates 1.5 times greater than that which occurs in nature. Nitrogen mineralization was not affected by simulated rain at pH 3.5 or 4.1 in soils exposed for 156 day at 2.3 times the natural rate of precipitation, for 27 or 81 day at 4.6 times the natural rate, for 54 day at 7.1 times the natural rate, or for 234 day at 15 times the natural rate. On the other hand, mineralization was fastest in soil exposed to pH 3.5 rain for 234 day at 4.6 times the natural rate of precipitation and for 81 day at 15 times the natural rate. Nitrate formation in soil amended with ammonium was inhibited by rain of pH 3.5 regardless of the intensity of rain or the duration of exposure. For a constant rate of rain application, the inhibition of nitrate formation in ammonium-amended soil generally increased with longer periods exposure. The data show that the use of different rates of additions of artificial rain or different periods of exposure to the simulated precipitation will lead to different conclusions on the influence of acid rain on N mineralization in soil.

1. Introduction

Investigations conducted under controlled conditions indicate that acid precipitation can alter the rates of N mineralization and nitrification in forest soils. These processes are important to forest productivity because inorganic N often limits plant growth in forest ecosystems (Auchmoody and Filip, 1973; Keeney, 1980). The need to predict the impact of long-term exposure of soil to acid precipitation has led to the use of techniques involving the input of H^+ at intensities greater than those that occur in nature, either by applying solutions containing unnaturally high concentrations of H^+ (Tamm *et al.*, 1977; Francis, 1982) or by adding solutions containing realistic levels of acidity at rates greater than occur in the field (Strayer *et al.*, 1981; Novick *et al.*, 1984).

Tamm and coworkers (1977) found that adding enough H_2SO_4 to a forest soil to lower its pH from 4.4 to 3.9 resulted in an increase in the quantity of inorganic N that accumulated during incubation. In contrast, Francis (1982) found that N mineralization was inhibited following the addition of concentrated H_2SO_4 to soil. Strayer *et al.* (1981) reported that the application of a solution of simulated rain at either high rates or at rates

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comparable to those observed in nature generally resulted in a stimulation of N mineralization. In another study of several forest soils, application of simulated acid rain for 24 weeks at a rate about 8 times greater than occurs in nature inhibited, stimulated, or had no effect on N mineralization (Novick *et al.*, 1984). Nitrate formation in ammonium-amended soil has been demonstrated to be sensitive to simulated acid rain (Novick *et al.*, 1984; Strayer *et al.*, 1981) or to solutions containing unnaturally high acidities (Francis, 1982).

It is not known whether simulated acid precipitation has the same influence on mineralization when applied at high rates in short periods or at low rates for longer periods of time. Such information is important if data from short-term studies are to be used to help predict the consequences of long-term exposures. A study was therefore conducted to determine the influence of the rate and duration of application of simulated acid rain on nitrogen mineralization and nitrification in a forest soil.

2. Materials and Methods

Soil was collected from a site in the Panther Lake watershed of the Adirondacks region of New York. The organic horizon (02) of an area of approximately 3 m^2 was sampled to a depth of 15 cm after the fresh litter at the soil surface was removed. The soil is a spodosol (coarse-loamy, mixed frigid Fragiorthod), and analyses by methods previously described (Novick *et al.*, 1984) showed that the organic layer has a pH of 3.9, 58.2% organic C, 3.01% organic N, and a cation exchange capacity of 154 meq per 100 g of dry soil.

Polyvinyl chloride cylinders (4 cm in diameter and 10 cm in height) were packed with 40 g of soil that previously had been passed through a 4-mm sieve. Simulated rain of pH 3.5, 4.1 or 5.6 was applied to each cylinder through a 10-μL capillary pipet that was attached directly to the bottom of a 150-mL plastic reservoir containing the simulated rain added to one cylinder of soil. The composition of the simulated rain has been previously described (Strayer and Alexander, 1981). The pH of this solution was 4.1, and it was adjusted to pH 3.5 with 1 N HCl or pH 5.6 with 1 N KOH. The soils were incubated at 21 °C.

Applications of 1.3, 1.9, 3.8, 5.8, or 11.5 cm per cylinder (16, 24, 48, 73, or 145 mL per cylinder, respectively) were made every 3 day. The solution was applied in a period of 30 to 165 min, depending on the volume of solution. These rates are equivalent to 1.5, 2.3, 4.6, 7.1, and 15 times that which the soil receives in the field. The cylinders that received 1.3, 3.8, or 11.5 cm of simulated rain per application were sampled after 27, 81, and 234 day of treatment. Cylinders that received applications of 1.9 or 5.8 cm of rain were sampled after 156 or 54 day of treatment, respectively. Because the average rate of precipitation in the Adirondacks region is 100 cm per year, the soil in this study was exposed to rates of precipitation equivalent to 1.5 to 15 times that which the soil would receive in the field.

After exposure to the simulated rain for the specified period of time, the soil from six replicate cylinders was pooled and mixed. To determine the rates of nitrification and

nitrogen mineralization, 5.0-g portions of the soil were placed in 50-mL Erlenmeyer flasks. The water content of the samples was adjusted to field capacity with distilled water or a solution of $(NH_4)_2SO_4$ (100 μg of N per g of dry soil). The flasks were covered with a polyethylene film to prevent moisture loss, and they were incubated at 28 °C. At intervals, 25 mL of 1.5 N K_2SO_4 was added to triplicate flasks of each treatment. Nitrate levels in the soil were determined 4 or 5 times in a period of about 30 day for soil incubated without ammonium and after 0, 4, and 8 day for soil amended with ammonium. Nitrate was analyzed by the chromotropic acid procedure (West and Ramachandran, 1966). Ammonium was measured by the method of Weatherburn (1957). Statistical analysis was performed using linear regression analysis as described by Kleinbaum and Kupper (1978). Significant differences are at $p < 0.05$.

3. Results

The number of rain applications and the total quantity of rain applied to the cylinders of each treatment are shown in Table I. One set of treatments received about 100 cm

TABLE I

Rates of nitrification in soil amended with 100 μg of ammonium nitrogen per g of soil after exposure to pH 3.5, 4.1, or 5.6 precipitation applied at different rates and for different periods of time

Duration of exposure (day)	Rate of rain application[a]	Total quantity of rain applied	Nitrate formation (μg N/g soil/day)			% Inhibition	
			pH 3.5	pH 4.1	pH 5.6	pH 3.5 vs pH 5.6	pH 4.1 vs pH 5.6
		cm					
27	1.5	11.7	14.2A[b]	14.0A	17.0B	16.2	17.6
	4.6	34.2	14.8A	14.7A	16.0A	7.5	8.1
	15	103.5	13.6A	14.4AB	15.3B	11.1	5.8
54	7.1	104.4	15.1A	17.3B	18.2B	17.0	4.9
81	1.5	35.1	15.8A	18.8B	18.6B	15.1	0
	4.6	102.6	15.2A	16.6AB	17.4B	12.6	4.5
	15	310.5	13.5A	14.3A	17.7B	23.7	19.2
156	2.3	98.8	14.9A	16.6B	17.5C	14.9	5.1
234	1.5	101.4	13.8A	9.5B	18.5C	25.4	48.6
	4.6	296.4	17.5A	18.4A	20.6B	15.0	10.7
	15	897.0	16.4A	19.2B	23.5C	30.2	18.3

[a] The natural rate of rainfall is considered to be 1.0.

[b] Values in the same row are not significantly different ($p < 0.05$) if followed by the same letter.

of simulated precipitation in different periods of time. This quantity of rain represents the amount the soil would receive in the field in 1 yr since the average precipitation in the Adirondacks region is about 100 cm annually. The other treatments provided approximately 0.1 to 9 times the quantity of precipitation that the soil would receive in the field.

Nitrate was the sole form of inorganic N found to accumulate in this acid forest soil. Ammonium levels remained below about 10 μg of N per g of soil, as was found for other soils collected from the same location (Klein *et al.*, 1984; Novick *et al.*, 1984). The rates of N mineralization in soil previously treated with 11.7, 34.2, or 103.5 cm of simulated precipitation in a 27-day period are shown in Figure 1. These rates of application are

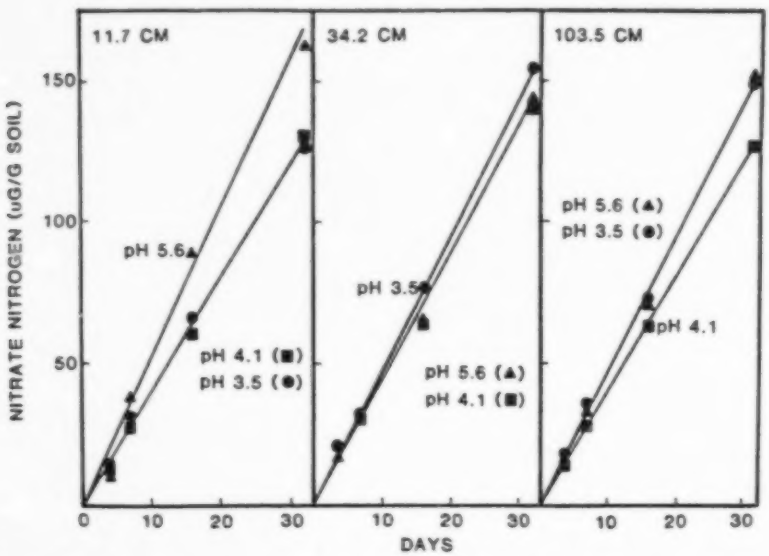

Fig. 1. Nitrate formation after treatment of soil for 27 day with 11.7, 34.2, or 103.5 cm of simulated precipitation at pH 3.5, 4.1, or 5.6.

1.5, 4.6, and 15 times the natural rate of exposure, respectively. The application of 11.7 cm of simulated precipitation at either pH 3.5 or 4.1 significantly inhibited mineralization. Treatment for 27 day with 34.2 cm of rain at the three pH values did not result in significant differences in the rates of mineralization. In soil receiving 103.5 cm of simulated rain at pH 4.1, N mineralization was significantly slower than in soil treated with either the pH 3.5 or pH 5.6 rain.

The application of 104.4 cm of rain in 54 day, which is about 7 times the natural rate, did not cause significant differences in the rates of N mineralization among the treatments of different acidities (Figure 2).

After treatment of the soil for 81 day with simulated rain, nitrate accumulation was slower after the application of 35.1 cm of simulated precipitation at pH 3.5 or 4.1 than at 5.6 (Figure 3). Mineralization in soils receiving larger volumes (102.6 or 310.5 cm) of either pH 3.5 or 4.1 rain applied in 81 day was not significantly different from that occurring in soil treated with the solution at pH 5.6, except that mineralization in soil treated with 310.5 cm of pH 3.5 rain was significantly faster than in soil previously

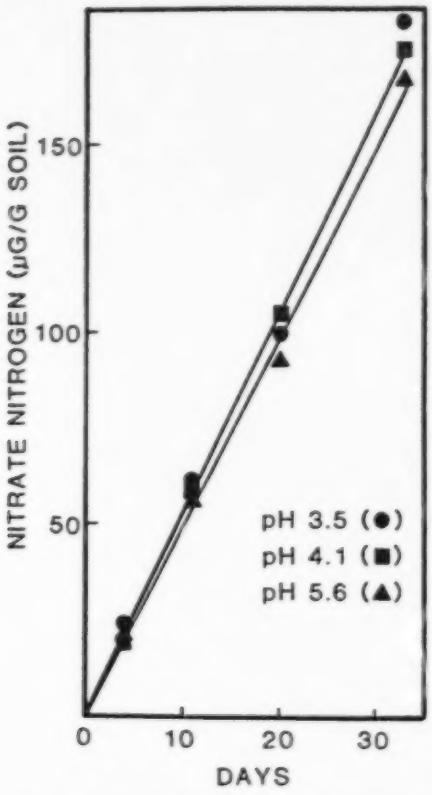

Fig. 2. Nitrate formation after treatment of soil for 54 day with 104.4 cm of simulated precipitation at pH 3.5, 4.1, or 5.6.

exposed to rain of lower acidity. Therefore, after treatment of the soil with simulated precipitation for 81 day, inhibitions of N mineralization by acid rain were noted only when rain applications were made at 1.5 times the ambient rate. Rain at pH 3.5 did not inhibit N mineralization in soil exposed to 4.6 or 15 times the natural rate of precipitation.

The soil was exposed to 98.8 cm of simulated rain in 156 day, which represents a rate of application equivalent to 2.3 times the natural rate. Nitrogen mineralization in soil so treated was not significantly affected by the pH of the rain (Figure 4).

Nitrogen mineralization was also determined in soil that received 101.4, 296.4, or 897.0 cm of simulated rain in 234 day. The rates of rain application were 1.5, 4.6, or 15 times those that occur naturally. Mineralization of N in soil that previously received 101.4 cm of precipitation at pH 3.5 or 4.1 was significantly less than in soil treated with the solution of pH 5.6 (Figure 5). Increasing the volume of solution applied to the soil to 296.4 or 897.0 cm did not result in increased depressions by the more acid treatments.

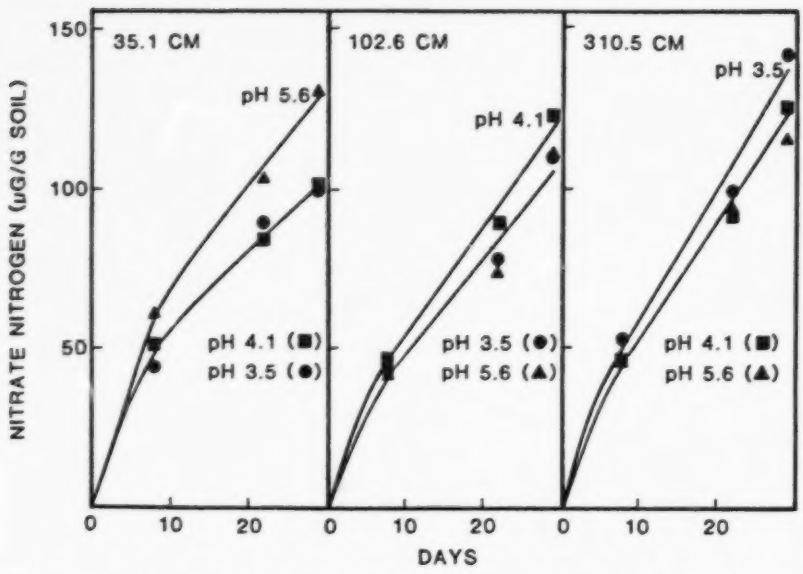

Fig. 3. Nitrate formation after treatment of soil for 81 day with 35.1, 102.6, or 310.5 cm of simulated precipitation at pH 3.5, 4.1, or 5.6.

In fact, N mineralization in soil that received 296.4 cm of pH 3.5 rain was significantly faster than if the pH of the solution was 4.1 or 5.6. The differences between pH treatments in soil receiving 897.0 cm of simulated rain were not statistically significant.

The effect of the rate and duration of rain application on nitrate formation in soil amended with 100 µg of ammonium N was also studied. Nitrate formation was measured for 8 day following treatment with the simulated rain. Nitrification rates were essentially linear with time during the 8-day period ($r \geq 0.970$). Nitrification was slower in soil previously treated with the solution at pH 3.5 than at pH 5.6 (Table I). The degree of inhibition by the rain at pH 3.5 depended on the duration of exposure. Inhibition by the pH 3.5 rain generally increased with increasing time of exposure. Although inhibition generally increased with the duration that the soil was exposed to the simulated rain, inhibitions were noted after the application of as little as 11.7 cm of rain at pH 3.5 or 4.1 in 27 day.

A comparison of the effects of pH 3.5 rain can be made among samples of soil that were treated with approximately the same quantity of rain for different periods of time. Thus, nitrification in soils that were treated with about 100 cm of pH 3.5 precipitation for 27, 54, 81, 156, or 234 day was 11.1, 17.0, 12.6, 14.9, and 25.4% slower, respectively, than in soil exposed to the same quantity of pH 5.6 precipitation. Nitrification in soil exposed to about 35 cm of pH 3.5 rain for 27 and 81 day was 7.5 and 15.1% slower, respectively, than in soil exposed to pH 5.6 rain. The same trend is not evident in soil receiving about 300 cm of rain.

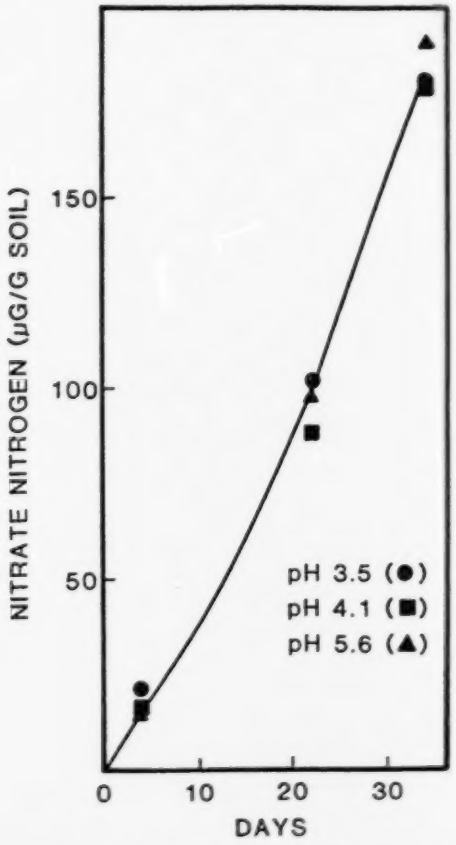

Fig. 4. Nitrate formation after treatment of soil for 156 day with 98.8 cm of simulated precipitation at pH 3.5, 4.1, or 5.6.

Differences in nitrification rates between the pH 4.1- and 5.6-treated soils were not apparent after 27, 54, or 81 day of treatment except for soil treated with 11.7 cm of rain in 27 day or 310.5 cm in 81 day (Table I). Nitrification rates were consistently slower in the soil treated with pH 4.1 than pH 5.6 rain after 156 or 234 day of exposure.

4. Discussion

In many studies of the effect of acid precipitation on microbial processes, simulated rainfall is added to soil at intensities or acidities greater than those that occur in nature. Such methods are used to allow for prediction of what may require long periods to occur in nature. The treatment of soil with solutions at unrealistically low pH levels is known to create artifacts (Tamm *et al.*, 1977). Although techniques that involve the application

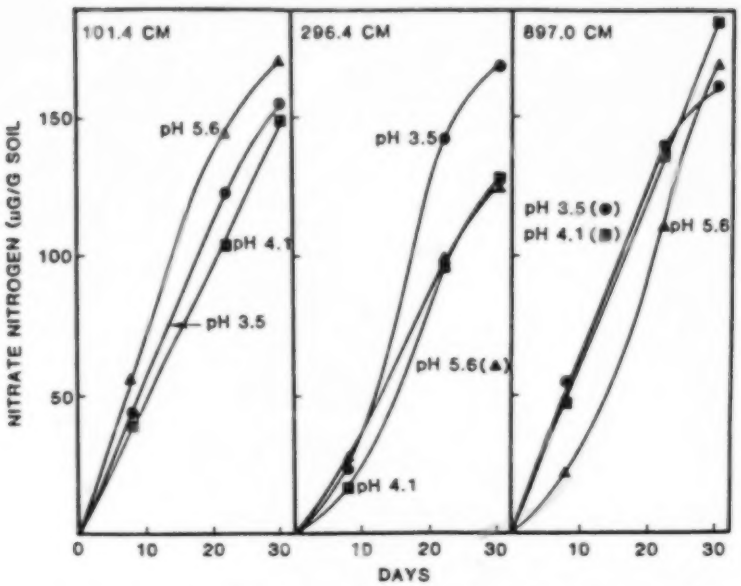

Fig. 5. Nitrate formation after treatment of soil for 234 day with 101.4, 296.4, or 897.0 cm of simulated precipitation at pH 3.5, 4.1, or 5.6.

of unrealistically large volumes of simulated rainfall at the pH levels observed in nature appear to be more realistic, the validity of this approach has not been evaluated heretofore. To assess its validity, the effects of varying the volume of rain and the duration that the soil was exposed to the rain were studied.

The results show that N mineralization in soil receiving simulated rain at rates 1.5 times greater than that in nature was slower at pH 3.5 and 4.1 than at 5.6, regardless of whether the rain was added in 27, 81, or 234 day. If the rain was applied at 4.6 times the natural rate, mineralization was unaffected by rain pH when the exposure was for 27 or 81 day and was enhanced by the rain at pH 3.5 if the exposure period was 235 day. If the rain was applied at 15 times the ambient rate, the effect of pH on N mineralization varied with the exposure, although the rate of mineralization in soil exposed to rain at pH 3.5 was always similar or faster than at the higher pH values.

Comparisons can also be made of the impact of the same *volume* of simulated rain applied in different periods of time. Considering volumes of about 35 cm, no effect of pH was evident if the treatment time was 27 day, but the more acid solutions were inhibitory if the time was 81 day. For volumes of about 100 cm, no effect was noted for exposure periods of 54, 81, and 156 day, but the more acid solutions inhibited the reaction if the treatment time was 234 day. On the other hand, for volumes of about 300 cm, N mineralization was fastest in soil receiving simulated rain at pH 3.5 for 81 or 234 day. Thus, the effects of pH when similar volumes are applied for different

periods of time are not always the same, but they do show a degree of consistency. The reason that the effects of rain pH on N mineralization differ when applied at different rates is not clear. Varying the quantity of rain applied to the soil may influence the level of potentially inhibitory factors present in the soil. Levels of toxic cations or organic compounds may be reduced by increasing the quantity of solution that passes through the soil. Different rates of rain application may also influence the quantity of organic matter available for mineralization (Killham and Firestone, 1982). Regardless of the reason, however, the lack of a consistent effect when similar volumes of simulated rain are applied to soil in different periods of time makes difficult the interpretation of the consequences of this stress.

In contrast to unamended soil, differences were consistent and readily apparent in the ammonium-amended soils. With the exception of the soil receiving 4.6 times the natural rate of rain addition for 27 day, nitrate formation in ammonium-supplemented soils was slower if the soil was exposed to rain at pH 3.5 than at pH 5.6, regardless of the exposure period, the rate of simulated rain application, or the total quantity of solution applied. With longer exposure periods, the data showed that the rates of nitrate accumulation in soil exposed to pH 4.1 rain were between the rates in soils treated with rain at pH 3.5 or 5.6. The greater sensitivity to inputs of simulated acid rain in soil amended with ammonium has been noted previously (Strayer *et al.*, 1981; Novick *et al.*, 1984).

Although the effects of simulated acid rain on N mineralization and nitrification are not necessarily similar in soils treated for different durations and with different quantities of rain, it is apparent that the acidity of precipitation can influence the rates of these important processes. The results show that, as compared to rain at pH 5.6, rain at pH 3.5 or 4.1 inhibited nitrification and N mineralization when applied at a rate 1.5 times greater than the soil receives in the field. Increasing the rate of application of simulated rain up to 15 times the ambient rate did not consistently lead to responses in N mineralization that were the same as at ambient rates. Thus, assessment of the influence of acid rain on N mineralization should be made using rates of application of simulated rain similar to rainfall rates that prevail in nature.

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